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# Surface Analysis of Reactive Ion Etched PZT Thin Films in $SF_6$ Plasma

by Eugene Zakar

**ARL-TR-4284** **September 2007**

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# Surface Analysis of Reactive Ion Etched PZT Thin Films In $SF_6$ Plasma

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Reactive ion etching of sol-gel deposited $Pb(Zr_{O.52}\ Ti_{0.48})0_3$ thin films was performed in $SF_6$ plasmas. Etch rate was determined as a function of cathode power and chamber pressure, attaining a value of 65 nm/min at 300 W. Auger electron spectroscopy measurements revealed an excess Pb 10 nm thin layer on as-deposited film surfaces. X -ray photoelectron spectroscopy measurements showed the existence of $ZrF_4$ and $PbS0_4$ species on etched surfaces, in addition to traces of S and F. These measurements also indicated that Ti is relatively easy to remove while Pb removal is the rate limiting step in the etch process.

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## 1. Introduction

Lead zirconate titanate [$Pb(Zr_xTi_{1-x})0_3$] (PZT) thin films usher in a new generation of sensor, actuator, memory, and microelectromechanical systems (MEMS) due to their superior piezoelectric properties. To incorporate/integrate these materials into silicon IC technology it is necessary to develop anisotropic dry etch processes to etch desired, precisely accurate and defect free PZT structures in the micrometer size range. One of the widely used dry etching processes is halogen plasmas - chlorine and fluorine based gases which have shown high potential to achieve the desired results (*1-14, 20*). However, selection of fluorine (*1*) or chlorine (*13*) chemistry requires extensive experimental analysis to understand the basic reaction chemistry. Most recently a mixture of fluorine and chlorine gases have been proposed for a clean etch profile of PZT films with a fast etch rate using high plasma density sources ECR (*21*), EDCR (*22*), and ICP (*23, 24*).

One of the simplest ways to understand the reactions underlying the plasma etching mechanism is the study of etching by-products on the surface of PZT. Analysis of PZT surfaces etched in various single halogen (e.g: Cl and F) molecules has been performed in the past using techniques such as x-ray photoelectron spectroscopy (XPS) (*3, 8-10, 13, 15*) to determine the presence and composition of surface reactant species. Recently $SF_6$ plasmas have been used successfully to etch PZT (*5, 6, 25-30*), since it is a non-toxic, stable gas and is widely used in IC manufacturing. To date, very little surface studies have been reported on PZT etched with $SF_6$. We report here about XPS, Auger electron spectroscopy (AES), and etch rate measurements performed on sol-gel deposited PZT films reactive ion etched (RIE) in $SF_6$ plasmas.

## 2. Experiment

Sol-gel $Pb(Zr_{0.52}Ti_{0.48})0_3$ solutions were spin coated onto the platinized Pt(170 nm)/Ta(20 nm)/$Si0_2$/Si wafers followed by crystallization using rapid thermal annealing at 700 °C to get the thin films 250-1000 nm. This is a very common structure used for PZT MEMS devices, where the Pt layer is the bottom electrode. Etching was performed in a PlasmaTherm 720 Shuttlelock RlE system with a standard parallel plate reactor design. Samples were patterned with AZ4330 photoresist and mounted on a liquid cooled cathode surrounded by an Ardel annular ring electrode shield material to enhance etch uniformity. XPS measurements were performed using a Physical Electronics model PHI 5800 system. AES measurements were performed using a Physical Electronics model PHI 600 scanning Auger microprobe.

## 3. Results

Constituents of PZT are comprised of heavy metals (Pb, Zr, Ti), and produce halide byproducts having low volatilities under normal $SF_6$ RIE conditions which may redeposit attributing to physical sputtering rather than chemical etching (*16*). Since etching of PZT films to low energy (30-40 eV) was found to produce etch yields that were greater than the expected sputter yields under the same conditions (*16*), this indicates that some chemical reaction may also be occurring in the fluorine plasmas. Figure 1 shows PZT etch rate as a function of cathode power for 30 mTorr and 50 mTorr chamber pressures. As power was increased from 100 W to 300 W, the etch rate increased from 15 nm to 65 nm/min, cathode bias increased from 25 V to 225 V. The rate increase with power is probably due to higher associated ion bombardment energies, which induce ion-assisted surface effects such as breaking of chemical bonds. This results in enhanced formation of reactant species, and the lowering of the desorption energy of these species. Etch rate increase could also be partly due to increased production of reactant fluorine species, although this is probably a secondary effect. Etch rate also increased as pressure was reduced. Since induced bias voltage is a measure of ion bombardment energy, the etch rate increase from the lower operating pressures further indicates that the etch process is dependent on ion bombardment effects.

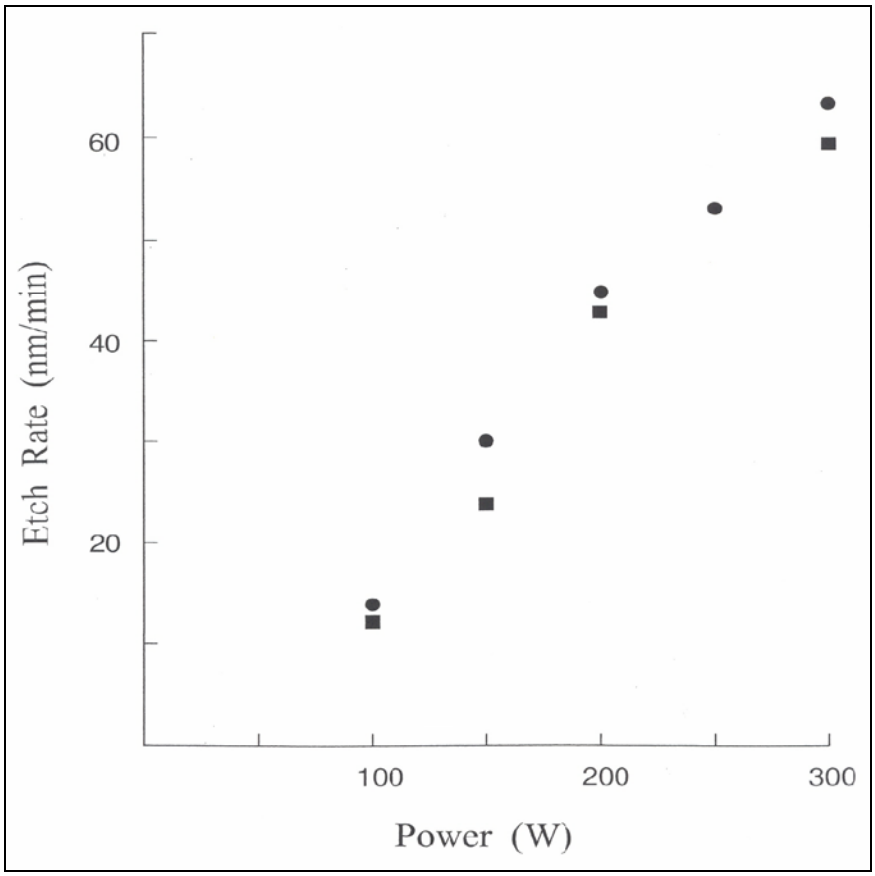


Figure 1. PZT etch rate as a function of power for pressures of 30 mT (■) and 50 mT (●), with 100 sccm $SF_6$ flow rate and 10 min. etch duration.

Figure 2 shows XPS data obtained on a PZT sample surface etched in $SF_6$ at a cathode power of 300W for 30 mT chamber pressure. The peak shown at 685.5 eV was not present prior to etching and corresponds to the formation of $ZrF_4$. This is a surface reactant species that would be expected to appear when etching PZT in fluorine-based plasmas. However, no evidence was seen of Pb or Ti based reactant species such as $PbF_2$ or $TiF_4$. Figure 3(a) shows the oxygen $0_{1S}$ peak at 531 eV from a PZT control sample, while figure 3(b) shows the same scan from a PZT sample etched in $SF_6$. The figure 3(b) data can be resolved into the sum of two peaks centered at 530.7 eV and 532.5 eV as shown. The peak at 530.7 eV corresponds to $TiO_2$ and $ZrO_2$ species, while the additional 532.5 eV peak indicates the presence of $PbSO_4$, a nonfluorine based chemical compound.

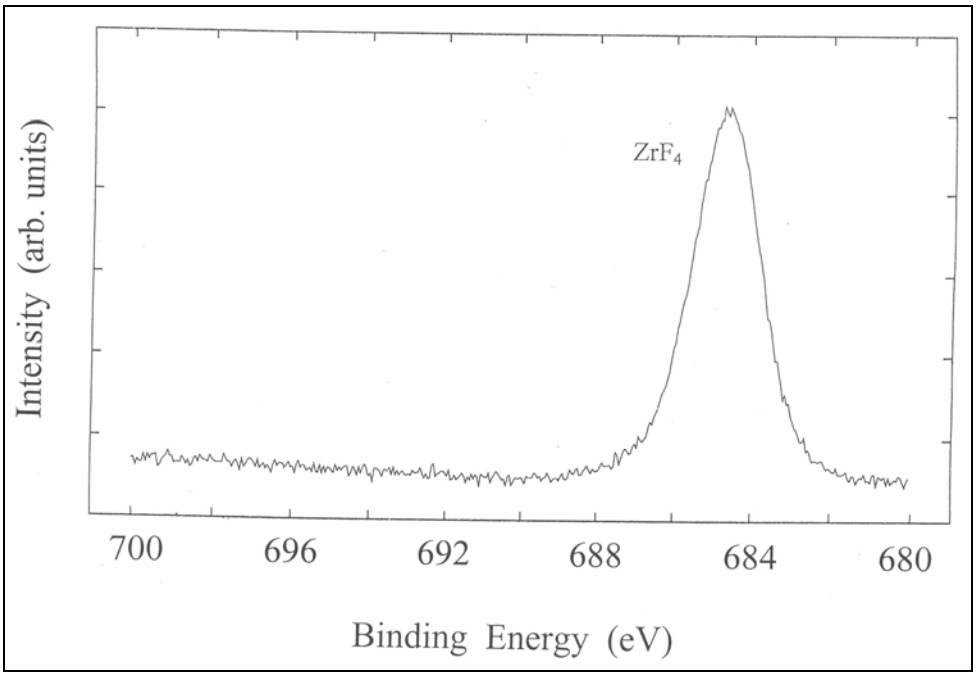


Figure 2. XPS scan showing appearance of $ZrF_4$ on PZT sample etched in $SF_6$ plasma.

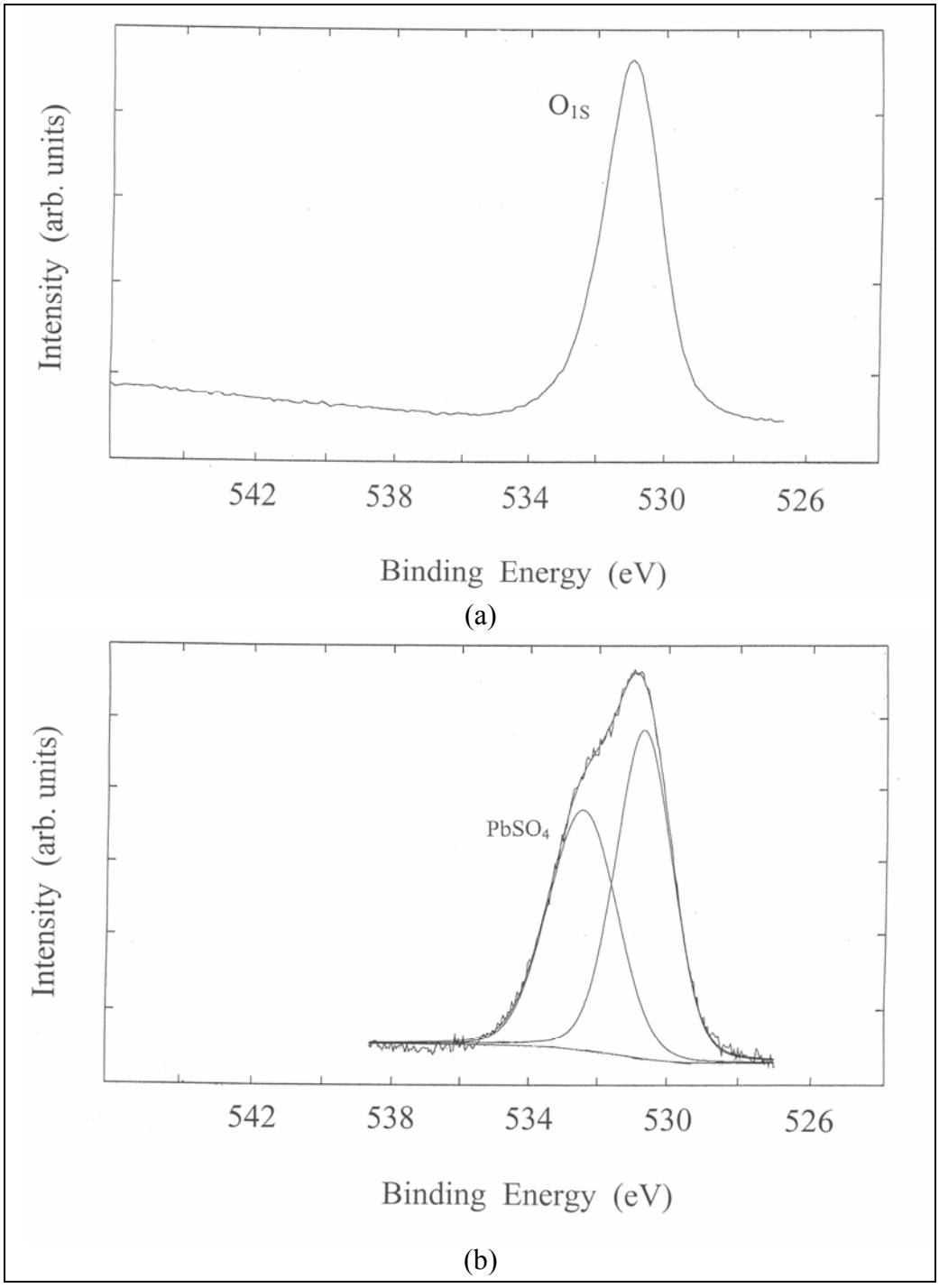


Figure 3. XPS scans of $O_{1S}$ data performed on (a) PZT control, and (b) $SF_6$ plasma etched samples.

AES measurements were performed on a control 0.25 μm PZT film sample sputtered with a 8 kV, 12 mA, Ar ion beam over a 200 μm square. Figure 4 shows the Pb atomic percent concentration as the film was sputtered through to the Pt under layer after about a 400s time duration. The film exhibited a Pb-rich surface region having an estimated thickness of 10 nm

and a concentration more than twice that of the bulk region. The Pb-rich surface regions similar to that observed here have been reported by others on PZT layers (*17-19*), and are thought to be an inherent result of thermal cycling of the deposited material, independent of the specific film deposition process. This non-ferroelectric surface region artifact can result in a reduced dielectric constant for the sample and may be detrimental to the operation of devices fabricated from PZT films.

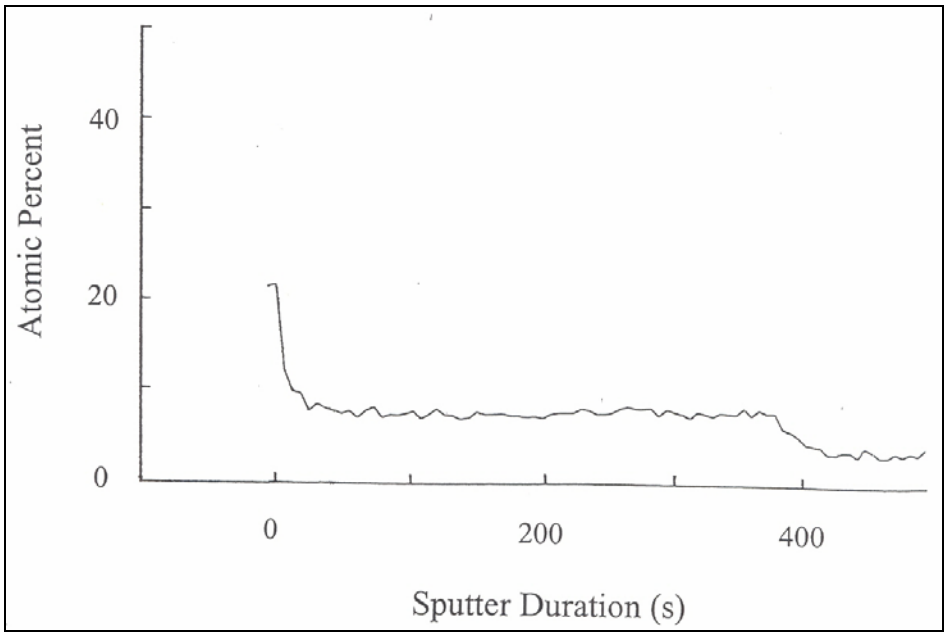


Figure 4. Pb concentration of 0.25 μm thick PZT sample determined from AES measurements as film was sputtered through to the Pt layer with 8 kV, 12 mA, Ar ion beam over a 200 μm square.

It is instructive to compare the Pb, Zr, and Ti components upon etching to provide an understanding of the etching mechanism. The relative atomic percentages of Pb, Zr, Ti, S, and F were estimated from XPS analysis for a control and an etched sample. The etched sample exhibited residual sulfur and fluorine compositions of 4.7% and 4.0%, respectively. Table 1 shows the relative atomic percentages of Pb, Zr, and Ti for both control and etched samples. Prior to performing XPS measurements on the control sample, the Pb-rich surface region was first sputtered through using an Ar ion beam so that a more valid initial surface composition could be obtained for comparison purposes. Table 1 shows that while the relative atomic percentages of Zr and Ti both decreased upon etching, the percentage of Pb increased, suggesting that Pb is the most difficult PZT component to remove. Other workers (*9,13,15,16*) have also reported that the removal of Pb is the rate limiting step for PZT etching in fluorine based plasmas. The formation of $PbSO_4$ during the etching process may add to the difficulty of Pb removal. In addition, table 1 shows that both the Ti/Pb and Ti/Zr ratios decreased upon etching, indicating that the Ti component of PZT is more easily removed than Pb or Zr in $SF_6$ plasmas. Similarly, Lin, et al. (*3*) found that Ti by-products were completely volatilized for RIE of PZT in

$CHF_3$ plasmas, while the fluorides of Pb and Zr were more difficult to remove. The above results are consistent with the fact that $PbF_2$ has a melting point of 855 °C, while $ZrF_4$ and $TiF_4$ sublime at 600 °C and 284 °C, respectively, (*16*) leading to the expectation that for PZT the Pb species would be most difficult to etch with the Ti species being most readily etched in $SF_6$ plasmas. In contrast, An, et al., (*l0*) found that the Pb component etched faster than Zr and Ti in chlorine based plasmas.

Table 1. XPS measurements of relative atomic percentages of Pb, Zr, and Ti for control and etched PZT samples.

| | **Pb** | **Zr** | **Ti** |
|---|---|---|---|
| Control | 10.1 | 10.9 | 8.5 |
| $SF_6$ Etched | 10.9 | 10.4 | 4.5 |

## 4. Conclusion

XPS and AES were used to analyze surface reaction and the by-products of the PZT RIE in $SF_6$. XPS measurements revealed the presence of $ZrF_4$ and $PbSO_4$, along with residual amounts of S and F. XPS measurements also indicated that Ti is readily removed from the PZT surface, while Pb removal is the rate limiting step in this etching process. AES measurements showed the presence of a Pb-rich surface region approximately 10 nm thick on as-deposited PZT material.

RIE rates of PZT in $SF_6$ plasma measured up to 65 nm/min at 300 W power. Conventional photoresist masking materials were used during the patterning and etch process, but more durable materials such as Pt, Ni, or $Si_3N_4$ can be used as a mask to improve the selectivity, etch rate, and may favorably influence the sidewall angle profiles of the etched PZT. There is a need to carefully monitor and control the amount of residual Pb and S that can redeposit on etched sidewalls of fabricated PZT thin film capacitor micro cells for Ferroelectric Random Access Memory (FRAM) applications.

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